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25

Patents Form 1/77

Patent Act 1977  
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21SEP98/E391140-2 D02224  
P01/7700-25.00/- 9820317.7

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(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

PA 98-06/MASS

2. Patent application number

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10 SEP 1998

9820317.7

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Martin Processing (UK) Limited,  
50 George Street,  
London W1A 2BB,

Patents ADP number (if you know it)

7517998001

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

PHOTOSENSITIVE ARTICLES

5. Name of your agent (if you have one)

J.Y. & G.W. Johnson

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Kingsbourne House,  
229-231 High Holborn,  
London WC1V 7DP

Patents ADP number (if you know it)

976001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

yes

- a) any applicant named in part 3 is not an inventor, or
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Description 8

Claim(s) 1

Abstract

Drawing(s)

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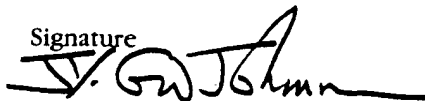
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11. I/We request the grant of a patent on the basis of this application.

Signature



Date 18.9.98.

12. Name and daytime telephone number of person to contact in the United Kingdom
- Mr. S. Hale  
0171 405 0356

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PHOTOSENSITIVE ARTICLES

This invention relates to polymeric films comprising photosensitive, particularly photochromic, organic compounds, which films exhibit a high response to exposure  
5 to electromagnetic radiation, particularly visible light, and to information storage devices incorporating such films.

As used herein, the unqualified expression "light" refers generally to electromagnetic radiation in the UV-visible region, and "colour" refers generally to the  
10 spectral properties within the UV-visible region of light or of an article.

WO-A-94/24785 discloses an information storage device comprising a photosensitive film for application to a small region of a monitor such as a television screen. The  
15 photosensitive material in the film may be photochromic. The photosensitive film may be metallised with gold or silver on its reverse side, both to guard the photosensitive material from light falling on the reverse side of the film, and to reflect light falling on the obverse side of the film but  
20 passing through the film without interacting with the photosensitive material back towards the photosensitive material. The film may be provided on its obverse side with a lens to focus light falling on the film and thus to yield a sharp image.

25

In some information-collecting applications, an image  
~~consisting of discrete spots (as opposed to a continuous~~  
image) may be found suitable. In such a case the obverse side of the film may advantageously be provided with a  
30 perforated mask, for example of cardboard, as focussing device instead of a plastics lens. The mask may be markedly thicker than the film, so that the photosensitive material is activated only by light falling on the storage device at a near-perpendicular angle to the film. The desirability of

employing a photosensitive material of high sensitivity will be appreciated, namely in order that a large colour difference between exposed and unexposed areas can be obtained in a short exposure time. However, there may be  
5 problems in reading the information which has been collected in a storage device of such construction. The reading step involves illumination with light of wavelength characteristic of the photosensitive material (unexposed or exposed) and analysis of the reflected light. If the  
10 photosensitive film is unreflective (either because the film has no backing or because the film has light-absorbent properties), the amount of reflected light is low. If the film is highly reflective, for example if it is metallised on its reverse side, the amount of reflected light is so  
15 great that it is difficult to distinguish between exposed and unexposed areas. The present invention addresses such problems.

According to the invention, there is provided a plastics film filled with a filler and having diffuse  
20 reflective properties, the film bearing a coating which contains a photosensitive organic compound.

The plastics film may be of conventional polymeric material such as regenerated cellulose, cellulose acetate or polyamide, although a polyester such as poly(ethylene  
25 terephthalate) may be preferred. The polymer desirably exhibits high transparency at relevant wavelengths.

The filler is preferably a pigment, more preferably a  
~~white pigment. Titanium dioxide (titania) is a particularly~~  
preferred white pigment for use when the photosensitive  
30 compound is chosen to react on exposure to visible light, because of its good diffuse reflective properties to visible light. Other common white pigments such as barium sulphate tend to confer a relatively high degree of specular reflection to visible light on a filled film, and they are  
35 accordingly less preferred. On the other hand, if the

compound is chosen to react on exposure to UV light, barium sulphate may be preferred to titania, because barium sulphate exhibits better diffuse reflectivity than titania to UV light. Other kinds of filler, for example polymer beads, may be employed. If an aerated or microvoided polymeric film is employed, the filler is generally a gas such as air. A decisive factor is that the refractive index of the filler particles (or voids) should differ from that of the polymer of the film so as to confer diffuse reflective properties on the film. The size and shape of the particles (or voids) may also be influential. The nature of the filler and filled film are not thought to affect the photochemistry of the photosensitive compound and accordingly are not thought to modify the nature of the information collecting step.

The diffuse and specular reflective properties of a film may be measured by conventional techniques, for example using a UV-visible spectrometer equipped with an integrating sphere for reflectance measurement and an optional light trap for removal of the specularly-reflected component. At relevant wavelengths, the plastics film preferably exhibits a diffuse reflectivity of at least 80%, more preferably at least 85%, and a specular reflectivity of no more than 5%, preferably of no more than 3% (all percentages being based on the reflectivity of a standard barium sulphate plate).

The coating may comprise more than one photosensitive organic compound. The photosensitive compound is preferably a photochromic compound. Photochromic organic compounds are known and include the photochromic fulgides and diarylethenes. Such compounds change colour when exposed to light whose wavelength corresponds to a spectral absorption peak of the compound. This colour change is the result of isomerisation, and it is reversed if the isomerised compound is exposed to light whose wavelength corresponds to a spectral absorption peak of the isomerised compound. The efficiency of the isomerisation reaction differs for

different compounds, depending on the efficiency with which the molecule absorbs photons and on the efficiency with which the molecule isomerises after absorption of a photon. The invention preferably employs a photochromic compound  
5 which reacts with a high degree of efficiency, most preferably in both the forward direction and the reverse direction. The photochromic compound preferably has a low tendency to thermochromism (colour change resulting from heat-induced isomerisation). The photochromic compound  
10 preferably strongly absorbs light from one or more of the RGB guns in a conventional television. A preferred compound is the fulgide Aberchrome 670 (Trade Mark of Aberchromics Ltd.) (CAS Registry No. 94856-25-4), which exhibits a rapid colour change (is rapidly bleached) by exposure to light of  
15 wavelength around 530 nm (corresponding to the green gun).

The coating preferably comprises a polymer in which the photosensitive compound is dispersed at molecular level. In general, any polymer compatible with the compound may be used. It will be appreciated that polymers which absorb  
20 light at relevant wavelengths, or which may react with the compound, or in which the compound may crystallise, will in general be unsuitable. An olefinic polymer such as polystyrene may generally be found suitable. The polymer of the coating desirably exhibits high transparency at relevant  
25 wavelengths. Coating compositions may be made for example by dissolving the polymer and compound in a solvent, and such compositions may be applied to the film by conventional techniques such as gravure printing or other printing methods.

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30 The film is preferably metallised on its reverse side. Metallisation serves primarily to guard the photosensitive compound from light falling on the reverse side of the film and secondarily to provide a reflective surface from which light passing through the film can be reflected back towards  
35 the photosensitive compound through the diffuse reflective film in the information collecting step. The efficiency of



light collection may in consequence be increased by some 10 or 20 percent.

The invention further provides an information storage device which comprises in combination the film described  
5 hereinabove and a perforated mask disposed on the coating-bearing side of the film. The mask may for example be perforated with holes of from 1 to 5 mm diameter. The thickness of the mask may for example be from 0.5 times to 2.5 times the diameter of the holes.

10 An information storage device according to the invention has the advantage that instrumental measurement of the colour of the film is markedly easier than in a device which incorporates a film which exhibits highly specular  
15 reflective properties or which exhibits little or no reflective properties. Measurement involves the analysis of light reflected from the film, and if the film exhibits excessive specular reflection the instrument may be swamped with reflected light owing to the fact that both the  
20 incident and the reflected light travel at near-perpendicular angle to the film.

Photosensitive compounds such as photochromic compounds are expensive materials. It is both economic and technically efficient to confine application of the photosensitive compound by applying the coating containing the  
25 photosensitive compound in the form of spots corresponding to the holes in the mask. The diameter of the spots is preferably larger than the diameter of the holes for maximum efficiency of light capture and to allow some latitude in registration.

30 The coating may comprise a small amount, for example 0.5 to 2% by weight, of a non-photosensitive light-absorbing compound. This has the advantage that the spots can be recognised instrumentally by spectral measurement at a fixed wavelength corresponding to an absorption peak of the non-

photosensitive compound, irrespective of the current colour of the photosensitive compound. If this compound absorbs visible light, the spots can be visually recognised even when the photosensitive compound is in visually colourless form. The non-photosensitive compound should be of low absorbance at wavelengths at which the photosensitive compound is of high absorbance in either isomeric state.

The invention is illustrated by the following Example, in which parts and proportions are by weight except where otherwise specified:-

#### Example

A coating composition was prepared by dissolving 17.98 g Aberchrome 670 (Trade Mark of Aberchromics Limited), 1.19 g Waxoline Yellow GFW (Trade Mark of BASF AG) and 53.94 g polystyrene (Lacqrene 1810, Trade Mark of Elf Atochem) in 327.64 g 70:30 toluene/methylethylketone. The composition was applied by gravure printing to a titania-filled polyethylene terephthalate film (Melinex 365, Trade Mark of Du Pont), which had been metallised on the heatseal side. (Melinex 365 comprises a filled poly(ethylene terephthalate) film 23 micron thick coated on one side with amorphous unfilled poly(ethylene isophthalate)/poly(ethylene terephthalate) 3 micron thick as heatseal layer. The heatseal layer is not thought to be of any relevance in the present invention.) The composition was applied in the form of circular spots of about 7 mm diameter. The spots were disposed in groups of 16, comprising concentric circles of 6 spots in an inner circle and 10 spots in an outer circle, the diameter of the outer circle being about 4 cm. The groups were disposed in regular square array at a density of about 310 groups per square metre. The total coating weight in the coated areas was 1.417 g/sq.m, of which 0.354 g/sq.m was Aberchrome 670. The film was also marked with registration marks to aid in subsequent laminating, stamping and slitting processes. On exposure to UV light (UV-A from

5 x 8W Philips Blacklight tubes), the spots turned from yellow to deep brown (colouration mode). The colour change was reversed (bleaching mode) by exposure to ambient room lighting in a short time of about 10 min.

5 An information storage device was made by joining together in the following order:

- (1) a paper backing layer;
- (2) the film described above, with its metallised surface towards the paper layer; and
- 10 (3) two layers of cardboard each 2 mm thick, perforated with 2.8 mm diameter holes corresponding to the spots on the film,

all being 40 mm diameter discs.

A similar film and device were prepared using a barium  
15 sulphate-filled poly(ethylene terephthalate) film (Melinex 329, Trade Mark of Du Pont). The instrumentally-measured difference between this device before and after exposure to a given amount of visible light was less than it was for the device containing the titania-filled film.

20 In a comparative experiment was tested an acetate film containing Aberchrome 670 in solid solution. The bleaching rate was slow in comparison with either of the filled films. It is thought that this was because the absence of a reflective backing resulted in less efficient photon  
25 capture.

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The specular and diffuse reflective properties of poly(ethylene terephthalate) films filled with titania and with barium sulphate were measured using a Perkin-Elmer Lambda 9 (Trade Mark) UV-visible-NIR spectrophotometer  
30 equipped with an integrating sphere for reflectance measurement and an optional light trap for removal of the specularly-reflected component. The results were expressed

as percentages of the reflectivity of a standard barium sulphate plate supplied by Perkin-Elmer. The relative amounts of specular and diffuse reflection were similar over the range from about 420 to 700 nm, although the total  
5 amount of reflection declined steadily with increasing wavelength. The following results were obtained at 560 nm:

Filler	Diffuse reflection %	Specular reflection %
Titania	85	2.5
Barium sulphate	83.5	5

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CLAIMS

1. A plastics film filled with a filler and having diffuse reflective properties, the film bearing a coating which contains a photosensitive organic compound.
  - 5      2. An information storage device which comprises in combination a film according to claim 1 and a perforated mask disposed on the coating-bearing side of the film.
-